Exchangeable Cation Hydration Properties Strongly Influence Soil Sorption of Nitroaromatic Compounds

Simone Charles, Brian J. Teppen, Hui Li, David A. Laird, and Stephen A. Boyd*

ABSTRACT

Nitroaromatic compounds (NACs) are commonly found as soil contaminants in military training sites and manufacturing facilities, and may adversely affect human and ecosystem health. Exchangeable cation effects on p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) sorption by the Webster (fine loamy, mixed, mesic Typic Haplaquoll) soil series A (WA) and B (WB) horizons were determined from batch sorption experiments. Smectite is the most abundant mineral in the horizons of this soil. Soil organic matter (SOM) removal increased p-NCB sorption to the WA and WB horizons by ~1.5 times, and increased 1,4-DNB sorption to the A and B horizons by ~1.2 to 2.2 times, respectively. Greater sorption of NACs by whole soils after SOM removal suggests that SOM suppresses p-NCB and 1,4-DNB sorption by soil mineral components. Clay ($<$2-μm fraction) removal decreased p-NCB sorption to the WA and WB horizons by ~8 and 11 times, respectively; clay removal decreased 1,4-DNB sorption to the WA and WB horizons by ~4.8 and 6.7 times, respectively. Nitroaromatic compound sorption to different soil fractions was measured to identify the independent effects of soil components and exchangeable cations on sorption. For this purpose, 1,2,4-trichlorobenzene (1,2,4-TCB) and 1,4-DNB sorption to two organic soils and a soil devoid of smectites, and p-NCB sorption to whole soil and the soil clay-sized fraction were determined. Exchangeable cation type was found to minimally affect sorption of 1,2,4-TCB, p-NCB, and 1,4-DNB by SOM. Sorption of p-NCB to homoionic soil clay-sized fractions was generally greater for clays saturated with monovalent cations than clays saturated with divalent cations. Greater p-NCB sorption followed decreases in cation hydration energy in the order $Na^+ < Li^+ << K^+ < Cs^+$ and $Ca^{2+} < Ba^{2+} < Mg^{2+}$. Similar trends were observed for whole-soil samples exchanged with these cations. This indicates that differences in nitroaromatic sorption are due to exchangeable cation effects on the clay mineral fraction.

NITROAROMATIC COMPOUNDS are commonly used as pesticides, explosives, and intermediates in the synthesis of dyes, ammunition, and solvents. Their uses and manufacture have resulted in contamination of soils, sediments, and aquifers at military training and manufacturing sites. Sorption processes play an important role in determining mobility, (bio)availability and, hence, persistence of NACs in soil. Clay minerals and SOM are generally considered to be the two most active soil components in the sorption of aqueous phase organic contaminants. For many nonpolar organic compounds, sorption is highly correlated with SOM content and is relatively independent of other sorbent properties (Chiou

et al., 1979, 1983; Karickhoff et al., 1979). In these instances, sorption has been conceptualized as solute partitioning into SOM (Chiou et al., 1979, 1983; Karickhoff et al., 1979). It has been further suggested that adsorption of such solutes by mineral fractions in soils is suppressed by the preferential adsorption of water (Chiou, 2002). However, many pesticides (e.g., triazines) and organic contaminants (e.g., NACs) containing polar functional groups are substantially adsorbed from bulk water by clays. In fact, comparison on a unit mass basis indicated that adsorption of NACs from water by smectite clays was greater than that by SOM (Sheng et al., 2001). Thus, clay minerals may play a dominant role in sorption of certain polar organic molecules, particularly for geosorbents with low SOM contents (Weissmahr et al., 1999).

Several studies have reported the high affinity of NACs for smectites in aqueous solution (Haderlein et al., 1996; Weissmahr et al., 1998; Boyd et al., 2001; Sheng et al., 2002; Johnston et al., 2001, 2002). This has been attributed to the formation of electron donor (clay)–acceptor (EDA) complexes facilitated by the electron withdrawing properties of the nitro (NO_2) group (Weissmahr et al., 1997). Alternatively, complexation of the NO_2 groups of NACs with exchangeable cations on the clay has been suggested as a primary sorption mechanism (Boyd et al., 2001). Partial solute dehydration associated with sorption in smectite interlayers with optimal distance (~12.3 Å) also provides favorable energy for adsorption (Boyd et al., 2001; Li et al., 2004b).

Sorption of NACs by reference smectite clays has been shown to be favored by weakly hydrated exchangeable cations such as K^+, NH_4^+, and Cs^+ and disfavored by more strongly hydrated cations such as Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+} (Haderlein and Schwarzenbach, 1993; Weissmahr et al., 1997; Boyd et al., 2001; Sheng et al., 2002). Cations that possess comparatively smaller hydrated radii manifest larger adsorption domains (i.e., unobscured siloxane surface) between exchange sites on clays. Weakly hydrated cations also have stronger interactions with the partial negative charge of the NO_2 groups in NACs (Boyd et al., 2001). Evidence for interactions between weakly hydrated exchangeable cations and NO_2 groups of NACs was provided by Johnston et al. (2002), who reported shifts in the NO_2

S. Charles, B.J. Teppen, H. Li, and S.A. Boyd, Dep. of Crop and Soil Sciences, and Environmental Science and Policy Program, Michigan State Univ., East Lansing, MI 48824; D.A. Laird, USDA-ARS, National Soil Tilth Lab., Ames, IA 50011. Received 25 July 2005. *Corresponding author (boyds@msu.edu).

Abbreviations: 1,2,4-TCB, 1,2,4-trichlorobenzene; 1,3,5-TNB, 1,3,5-trinitrobenzene; 1,4-DNB, 1,4-dinitrobenzene; BL, Brookston loam; C_e, equilibrium solute concentration; CEC, cation exchange capacity; C_i, initial solute concentration; DNOC, 4,6-dinitro-o-cresol; FeOx, iron oxides; HM, Houghton muck; HPLC, high-performance liquid chromatography; MSU, Michigan State University; NAC, nitroaromatic compound; NOCs, neutral organic contaminants; SOM, soil organic matter; p-NCB, 1-nitro-4-cyanobenzene; PP, Pahokee peat; WA, The Webster soil series horizon A; WB, The Webster soil series horizon B; XRD, x-ray diffraction.

vibrational modes of 1,3,5-trinitrobenzene (1,3,5-TNB) on adsorption by K^+–smectite. These shifts were not observed for smectites saturated with more strongly hydrated cations (i.e., Na^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}). Overall, cation hydration seems to be a central determinant of NAC sorption by smectite clays. Sorption of NACs occurs primarily in the interlayers of these clays, and cation hydration determines the interlayer distances, the effective size of adsorption domains between cations, and the ability of NO_2 groups to complex directly with exchangeable cations (Boyd et al., 2001; Johnston et al., 2001, 2002; Sheng et al., 2002; Li et al., 2004b).

Although the effect of cation saturation on NAC sorption by homoionic clays is well documented, little is known about the effect of exchangeable cation type on NAC sorption by surface soils or their effects on the relative contributions of soil organic and mineral components to the overall sorption. The objective of this study was to evaluate the contributions of SOM and mineral fractions as well as the effect of exchangeable cation type on NAC sorption by whole soil, SOM, and the soil clay-mineral fraction.

MATERIALS AND METHODS

The A and B horizons of the Webster clay loam soil were fractionated following standard procedures (Kunze and Dixon, 1986). Carbonates, SOM, iron oxides (FeO_x), and clay-sized particles were sequentially removed from each soil horizon. Carbonates were removed using 0.5 M sodium acetate acidified to pH 5 at 80°C, followed by the removal of SOM using 30% (v/v) H_2O_2 at 80°C, followed by the removal of free FeO_x using the citrate–bicarbonate–dithionite method. The clay-sized fraction (<2.0 μm) was obtained by wet sedimentation from the carbonate-OM-FeO_x–removed fraction (Whittig and Allardice, 1987). The fraction remaining after the removal of carbonates, SOM, FeO_x, and clay-sized particles was termed the residual sand plus silt fraction. The masses of carbonates and FeO_x removed, and residual sand plus silt fraction remaining were determined gravimetrically. Additional soils used (but not fractionated) were Pahokee peat (PP; euic, hyperthermic Lithic Haplosaprists), Houghton muck (HM; euic, mesic Typic Haplosaprist), and Brookston loam (BL; fine-loamy, mixed, superactive, mesic Typic Argiaquoll). The SOM content of whole soils and the amount of SOM remaining after extraction using H_2O_2 were determined by the Michigan State University (MSU) Soil Testing Laboratory using dry combustion and a Leco carbon analyzer (Leco Corp., St. Joseph, MI) (Nelson and Sommers, 1996). The content of clay-sized particles in the Webster soils was determined by the MSU Soil Testing Laboratory using the hydrometer method (Gee and Bauder, 1986).

To prepare homoionic sorbents, soil and soil fractions (100 g) were washed with 200 mL of 0.1 M solution of the cation chloride salt overnight, thereafter centrifuged and the supernatant discarded; this procedure was repeated five times. The soils were then washed with approximately 200 mL of Millipore Milli-Q (Billerica, MA) deionized H_2O, thereafter centrifuged and the supernatant tested with $AgNO_3$; the procedure was repeated until a negative Cl^- test with $AgNO_3$ was obtained. The soils were then freeze-dried and stored at room temperature (23 ± 1°C) until used.

p-NCB, 1,4-DNB, and 1,2,4-TCB were purchased from Aldrich Chemical Co. (Milwaukee, WI) with purities of 97, 98,

and 99%, respectively, and used as received. The water solubilities (S_w) of p-NCB, 1,4-DNB, and 1,2,4-TCB at 25°C are 1650, 69, and 49 mg L^{-1}, respectively, and the log K_{ow} values are 1.19, 1.46, and 4.02, respectively (Howard and Meylan, 1997).

Sorption of solutes by homoionic soil and soil fractions were measured in triplicate using a batch equilibrium technique. This involved adding aqueous solutions of p-NCB, 1,4-DNB, or 1,2,4-TCB over a range of initial concentrations (C_i, 1–42 mg L^{-1} for p-NCB and 1,4-DNB; 1–30 mg L^{-1} for 1,2,4-TCB) to a known mass of soil (0.1–0.4 g for p-NCB and 1,4-DNB; 0.04–0.35 g for 1,2,4-TCB). Initial solutions of the compounds were prepared in 0.05 M solution of the cation chloride salt. Total initial volumes of 5 mL (p-NCB, 1,4-DNB) or 7 mL (TCB) were pipetted into 7.5-mL borosilicate glass vials containing sorbent. The vials were rotated continuously overnight (24 h) in the dark at room temperature (23 ± 1°C); preliminary studies showed equilibrium was reached within 24 h (data not provided). The liquid and solid phases were separated by centrifugation at 4068 × g for 40 min, and the solute equilibrium aqueous concentration (C_e) measured using a PerkinElmer high-performance liquid chromatograph (HPLC) system (PerkinElmer, Norwalk, CT). This instrument consisted of a binary liquid chromatography pump (Model 250) with a series 200 autosampler and a series 200 UV-visible detector which was set at 254, 262, and 228 nm for p-NCB, 1,4-DNB, and 1,2,4-TCB, respectively. An Alltech platinum EPS C18 column (Deerfield, Illinois) was used for determining p-NCB and 1,4-DNB. A Varian microsorb-MV C18 column (Palo Alto, CA) was used for determining 1,2,4-TCB. The mobile phase was an isocratic mixture of methanol (HPLC grade) and Milli-Q deionized water (methanol/water ratios of 55:45 for p-NCB, 65:35 for 1,4-DNB, and 92:8 for 1,2,4-TCB) with a flow rate of 1.0 mL min^{-1}. The amount of solute sorbed was calculated from the difference between C_i and C_e. Compound recoveries in control vials without sorbent were >95%; because of the high solute recoveries, the data (C_i) were not adjusted.

The effect of exchangeable cation type on NAC sorption by SOM was evaluated using either organic soils relatively devoid of mineral matter (PP and HM) or a mineral soil devoid of swelling clays (i.e., smectites) (BL). The PP was purchased from the International Humic Substances Society (Denver, CO). The BL was obtained from Ionia, Michigan, and the HM from Bath, MI. Sorption isotherms for p-NCB and 1,4-DNB, and 1,2,4-TCB by these soils were obtained using the batch equilibrium technique described above. These soils were saturated with K^+ or Mg^{2+} to evaluate the effect of cation type on sorption of NOCs.

The whole WA and its isolated clay-sized fraction were saturated with different exchangeable cations (Cs^+, K^+, Na^+, Li^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) to determine the effect of exchangeable cation on sorption of p-NCB. Batch equilibrium experiments were conducted using the cation-saturated soil clay fractions and the whole soils with p-NCB as the sorbate. Sorption of p-NCB by K^+-saturated reference clays which are representative of the identified clay types in the soil clay fraction (see below) were also measured using batch equilibrium experiments as described above. The clays used were: Wyoming montmorillonite (SWy-2), illite (IMt-2), and kaolinite (KGa-2) obtained from the Clay Minerals Society Source Clay Repository (Dep. of Agronomy, Purdue University, West Lafayette, IN) and beidellite from Ward's Natural Science (Rochester, NY).

X-ray diffraction (XRD) was used to identify the clay mineralogy of the Webster soil samples (Fig. 1) (Whittig and Allardice, 1987). Oriented samples of Mg^{2+}– and K^+–saturated soil clay-sized fractions were prepared by dropping
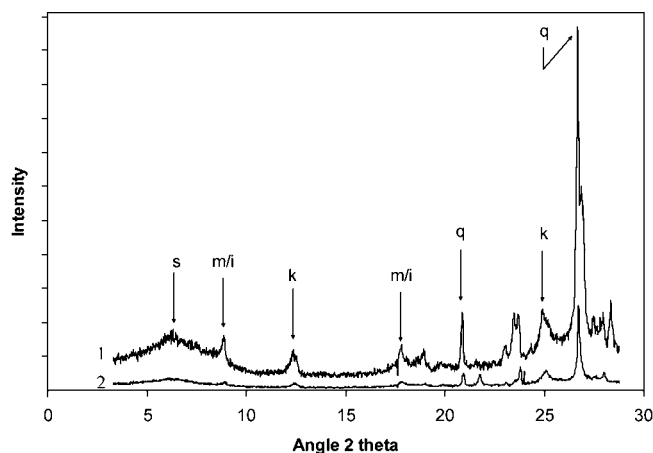
Fig. 1. X-ray spectra of clay-sized fractions of the Webster soil series horizon A (1) and horizon B (2) saturated with Mg^{2+} were obtained using air dried films (s, smectite; m/i, mica and/or illite; k, kaolinite; q, quartz).

suspensions of the clay-sized materials on glass slides, then air-drying. Clay films were also heated at 500°C and treated with ethylene glycol for confirmation of types of clay minerals present. Samples were analyzed using CuKα radiation and a Philips APD 3720 X-ray diffractometer (Philips Electronic Instruments, NJ).

The amount of smectite in the Webster soils was estimated using the cation exchange capacity (CEC) of the whole soil which was measured using the ammonium acetate method (Sumner and Miller, 1996), assuming that the CEC of the soil originated solely from SOM and soil smectites. The CEC values for the soil smectites and SOM were 120 and 160 cmol kg^{-1}, respectively:

$$CEC = (160 \text{ cmol kg}^{-1})(f_{om}) + (120 \text{ cmol kg}^{-1})(f_{cm}) \quad [1]$$

where f_{om} and f_{cm} are the fractional SOM and smectite clay contents of the soil. For comparison, Laird et al. (1994) reported that the dominant clay mineral in another Webster soil was beidellite with CEC of 125 cmol kg^{-1}. To validate the smectite contents estimated by Eq. [1], we compared the XRD peak areas corresponding to each nonsmectite clay mineral with the smectite peak area, then estimated the relative fractional amounts of each nonsmectite clay mineral present in the clay-sized fraction as a fraction of the smectite peak (e.g., illite/mica, 0.125 and kaolinite, 0.125). Multiplying the percentage of smectite in the soil obtained using Eq. [1] (e.g., 24%) by the relative peak areas from the XRD results, we calculated the amount of non-smectite clay minerals (e.g., 3% illite/mica and 3% kaolinite). We subtracted the estimated smectite content (e.g., 24%) from the total clay content (e.g., 31%) to obtain the amount of nonsmectite clay (e.g., 7%) and compared this value to the sum of the non-smectite clay minerals estimated using the peak areas (3 + 3%).

Statistical Analysis

The sorption coefficients (K_f) and the constants related to the sorption isotherm curvature (n) were estimated using the Freundlich equation, $Q = K_f C_e^n$, where Q is the sorbed solute concentration per unit mass of the sorbent (mg g^{-1}), K_f is the sorption coefficient (mg g^{-1})[mg L^{-1}]$^{-n}$, and n is a constant related to the isotherm curvature (concave or convex). Comparisons of sorption isotherms were made by comparing the K_f

and n values for each soil-solute system using SAS (SAS Institute, 1999). A significant difference between isotherms was assigned when there was a significant difference (α = 0.05) between both the K_f and n values for compared isotherms or between only the K_f values of compared isotherms (Laboski and Lamb, 2004).

RESULTS AND DISCUSSION

The Webster soil contains smectite as its most abundant clay mineral (Fig. 1), in agreement with previous results for other samples of the Webster soil (Laird et al., 1994). The smectite contents of the WA and WB horizon soils, estimated using the CECs of the soils and XRD data, were approximately 24 and 16%, respectively (Table 1). The SOM contents of the WA and WB horizons were 3.2 and 1.3%, respectively (Table 1). The other soils studied (PP, HM, BL) had much higher SOM contents (73.2, 43.2, and 9.4%, respectively) (Table 1) and were devoid of smectite clays implicated in the mineral phase sorption of NACs.

When K$^+$ was used as the saturating exchangeable cation, the relative contributions of SOM and clays to NAC sorption can be easily distinguished. Removal of SOM from the WA and WB horizon soils increased sorption of p-NCB and 1,4-DNB by factors of 1.2 and 2.2 (calculated at Ce = 5 mg L^{-1}), respectively (Fig. 2 and 3). For the whole soil samples, it appeared that the overall effect of SOM was to suppress sorption of p-NCB and 1,4-DNB, though SOM itself is undoubtedly a sorptive sink for these compounds. Karickhoff (1984) proposed that, if SOM blocked clay sorption sites, then SOM removal could result in increased sorption by clays. This effect for neutral organic contaminants (NOCs) and pesticides had not been demonstrated experimentally until now. Removal of the clay-sized fraction from the Webster soil samples decreased sorption of p-NCB and 1,4-DNB by factors of 4.8 to 11 (calculated at Ce = 5 mg L^{-1}), respectively (Fig. 2 and 3). Nitroaromatic compounds sorption by free FeO$_x$ was very low (data not reported) and the high affinity of smectites for NACs has been established (Boyd et al., 2001; Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Li et al., 2003; Johnston et al. (2001) and 2002; Sheng et al., 2002; Weissmahr et al., 1997). Therefore, our data support the premise that SOM and soil clays are the two soil components that dominantly influence NAC sorption.

Table 1. Measured soil organic matter (SOM), clay content, and cation exchange capacity (CEC) for the Webster soil series horizon A and B (whole soils, WA and WB, and soils from which SOM was removed, WAO and WBO), Pahokee peat (PP), Houghton muck (HM), and Brookston loam (BL) soils.

Soil†	Texture	%OM	%clay	%smectite	CEC
					cmol kg^{-1}
PP	Organic	73.2	–	–	–
HM	Organic	43.7	–	–	126
BL	Sandy clay loam	9.4	24	–	18
WA	Clay loam	3.2	31	24	35
WB	Clay loam	1.3	31	16	23
WAO	Clay loam	0.3	31	24	–
WBO	Clay loam	0.4	31	16	–

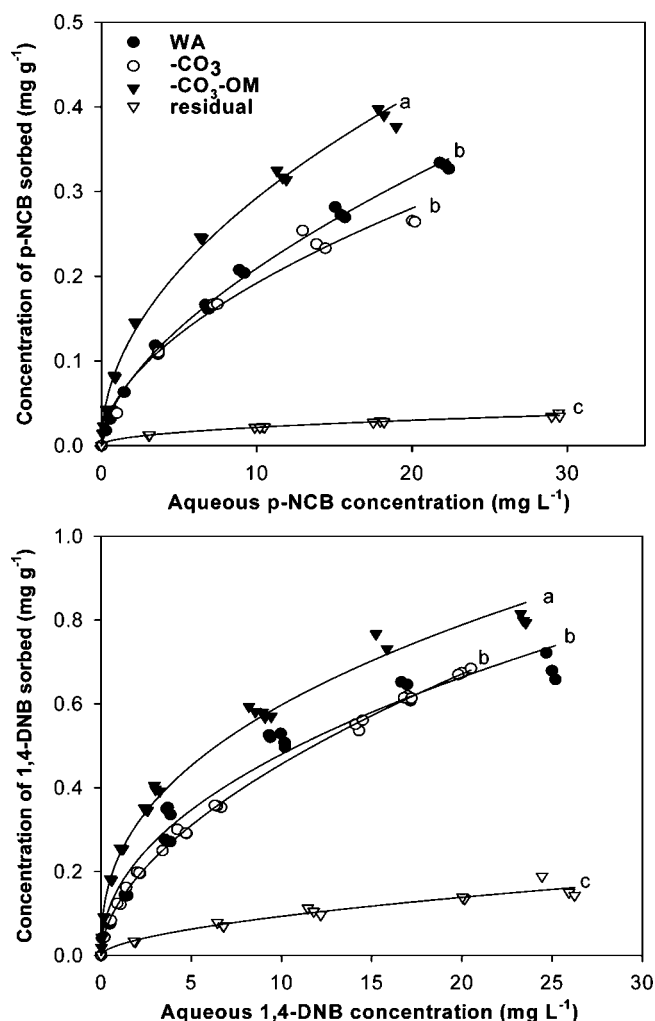† WAO = Webster horizon A soil with SOM removed, and WBO = Webster horizon B soil with SOM removed.

Fig. 2. Sorption isotherms for p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) by the K^+–saturated Webster A horizon soil (WA) and soil fractions: carbonates removed (-CO_3), carbonates and soil OM removed (-CO_3–OM), and the residual sand + silt fraction remaining after removal of carbonates, OM, free FeO_x and clay. Isotherms with different letters (a, b, c) are statistically different at $p < 0.05$.

Fig. 3. Sorption isotherms for p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) by the K^+–saturated Webster B horizon soil (WB) and soil fractions: carbonates removed (-CO_3), carbonates and soil OM removed (-CO_3–OM), and the residual sand + silt fraction remaining after removal of carbonates, SOM, free FeO_x and clay. Isotherms with different letters (a, b, c) are statistically different at $p < 0.05$.

When K^+ was the saturating cation in a smectitic soil, the contribution by soil clays to sorption of p-NCB and 1,4-DNB was far greater than the contribution by SOM. In fact, the masking of soil clay surfaces by SOM appears to be the greatest (albeit negative) effect on NAC sorption. The contribution of carbonates and the residual sand + silt fraction to sorption of the solutes was minimal for all soils (Fig. 2 and 3) which is consistent with the low carbonate levels we found in the whole soils (data not shown). This agrees with the findings of Laird et al. (1994) for another Webster soil.

The influence of exchangeable cation type on organic solute sorption to soil will depend primarily on how cations influence SOM and clay sorptive properties. Sorption of nonpolar compound 1,2,4-TCB by soils results predominately (if not exclusively) from partitioning into SOM (Chiou, 2002), and hence can be used to probe exchangeable cation effects on sorption by SOM. The isotherms for 1,2,4-TCB sorption by K^+– and
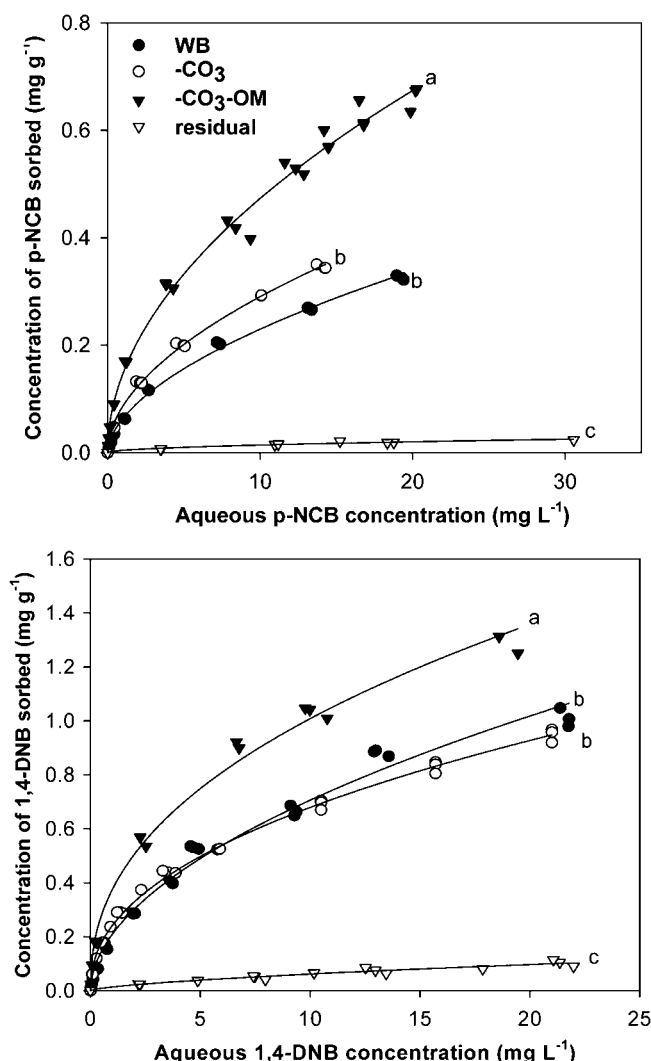
Mg^{2+}–saturated organic soils and BL were not significantly different (Fig. 4). Likewise, the 1,2,4-TCB isotherms for the K^+–saturated soils were not significantly different from those by Mg^{2+}–saturated WA or WB soils after SOM removal (Fig. 4). Other differences in sorption between K^+– and Mg^{2+}–saturated soils, though statistically significant at $p < 0.05$, were of small magnitude compared to the overall extent of uptake by each soil. The concentrations (Q_{om}) of 1,2,4-TCB sorbed per unit mass of SOM by the K^+–saturated HM, BL, and Webster soil samples were calculated at an C_e of 5 mg L^{-1} using the Freundlich K_f and n parameters (Table 2). The data were normalized to the amount of SOM as follows: $Q_{om} = K_f \times C_e^n/f_{om}$, where f_{om} is the SOM fraction (Table 1). The Q_{om} values for 1,2,4-TCB at a specific C_e among the K^+–saturated test soils differed by a factor <2 from 2.15 to 3.60 mg g^{-1} (Table 3). The Q_{om}
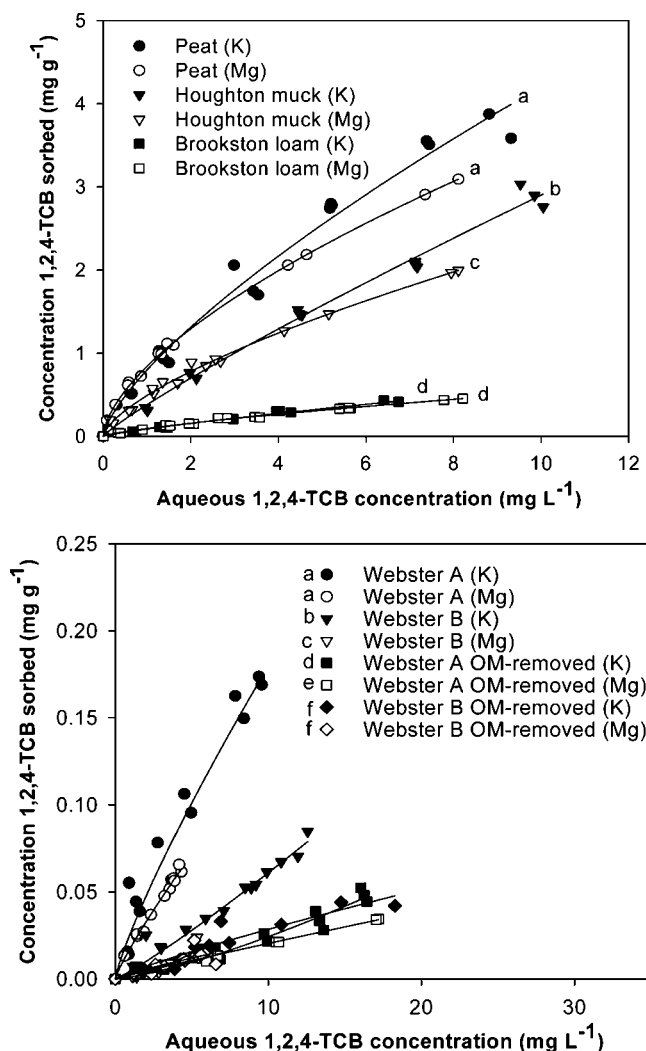
Fig. 4. Sorption isotherms for sorption of 1,2,4-trichlorobenzene (1,2,4-TCB) by K^+– and Mg^{2+}–saturated Pahokee peat, Houghton muck, and Brookston loam, the Webster A and B horizon soils, and the fractions with OM removed. Isotherm labels with different letters (a–f) represent statistical difference at $p < 0.05$.

values among the Mg^{2+}–saturated test soils varied by a factor of ~3 from 1.15 to 3.51 (Table 3). These Q_{om} values fall easily within the normal variation of K_{om} values

Table 3. Q_{om} values (calculated at $C_e = 5$ mg L^{-1} using the Freundlich sorption isotherms of Table 2) for 1,2,4-trichlorobenzene (1,2,4-TCB), p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) sorption by K^+- and Mg^{2+}–saturated soils. Q_{om} = amount of solute sorbed per unit mass of sorbent (Q)/fractional SOM content of sorbent. The ratio of the Q_{om} values for sorption of solute by K^+-saturated to that by Mg^{2+}–saturated soils (K/Mg) is also given.

	Q_{om}, mg solute g^{-1} SOM								
	1,2,4-TCB			p-NCB			1,4-DNB		
Soil†	K^+	Mg^{2+}	K/Mg	K^+	Mg^{2+}	K/Mg	K^+	Mg^{2+}	K/Mg
PP	3.48	3.13	1.1	1.07	0.55	1.9	1.10	0.62	1.8
HM	3.52	3.33	1.1	0.56	0.38	1.5	0.56	0.47	1.2
BL	3.60	3.30	1.1	0.65	0.46	1.4	1.36	0.61	2.2
WA	3.16	2.24	1.4	na‡	na	na	na	na	na
WB	2.15	1.15	1.9	na	na	na	na	na	na
WAO	3.22	3.51	0.9	na	na	na	na	na	na
WBO	3.46	3.02	1.1	na	na	na	na	na	na

† PP = Pahokee peat, HM = Houghton muck, BL = Brookston loam, WA = Webster horizon A soil, WAO = Webster horizon A soil with SOM removed, WB = Webster horizon B soil, and WBO = Webster horizon B soil with SOM removed.
‡ na, not applicable because sorption is dominated by clay minerals rather than SOM.

of nonpolar organic compounds observed among different soils from widely different geographical origins (Kile et al., 1995). The small variation in Q_{om} values observed here suggests that SOM was the dominant sorbent phase for 1,2,4-TCB, and that SOM functioned very similarly in this regard among the soils tested. Comparing 1,2,4-TCB sorption by each K^+– and Mg^{2+}–saturated test soil, the Q_{om} values were within a factor <2 of each other (Table 3), within normal variation of K_{om} values observed by Kile et al. (1995).

Nitroaromatic compounds are sorbed by both SOM and certain soil clays, most importantly smectites. Cation effects on NAC sorption by SOM can best be evaluated using soils devoid of such swelling clays. In general, the sorption isotherms for p-NCB and 1,4-DNB sorption by K^+–saturated HM and BL (both devoid of smectites) were not significantly different from those for sorption by the Mg^{2+}–saturated sorbents (Fig. 5). For both p-NCB and 1,4-DNB, sorption by K^+-saturated peat was greater than that by Mg^{2+}–saturated peat (Fig. 5). The Q_{om} values (calculated at $C_e = 5$ mg L^{-1}) for sorption by K^+-saturated peat, HM and BL fell within

Table 2. Freundlich equation K_f [(mg g^{-1})(mg L^{-1})^n] and n values for sorption of 1,2,4-trichlorobenzene (1,2,4-TCB), p-nitrocyanobenzene (p-NCB), and 1,4-dinitrobenzene (1,4-DNB) by K^+- and Mg^{2+}–saturated soils. The Freundlich equation fittings utilized sorbed concentrations normalized to fractional SOM content.

	1,2,4-TCB				p-NCB				1,4-DNB			
	K^+		Mg^{2+}		K^+		Mg^{2+}		K^+		Mg^{2+}	
Soil†	K_f	n	K_f	n	K_f	n	K_f	n	K_f	n	K_f	n
PP	1.09	0.723	1.15	0.622	0.585	0.374	0.212	0.590	0.586	0.391	0.225	0.631
HM	0.933	0.825	0.997	0.749	0.305	0.382	0.137	0.633	0.282	0.426	0.262	0.365
BL	0.868	0.884	1.12	0.671	0.273	0.534	0.194	0.539	0.934	0.231	0.314	0.415
WA	0.831	0.831	0.465	0.857	na‡	na	na	na	na	na	na	na
WB	0.354	1.12	0.085	1.62	na	na	na	na	na	na	na	na
WAO	0.377	1.33	0.959	0.805	na	na	na	na	na	na	na	na
WBO	0.418	1.31	0.585	1.02	na	na	na	na	na	na	na	na

† PP = Pahokee peat, HM = Houghton muck, BL = Brookston loam, WA = Webster horizon A soil, WAO = Webster horizon A soil with SOM removed, WB = Webster horizon B soil, and WBO = Webster horizon B soil with SOM removed.
‡ na, not applicable because sorption is dominated by clay minerals rather than SOM.
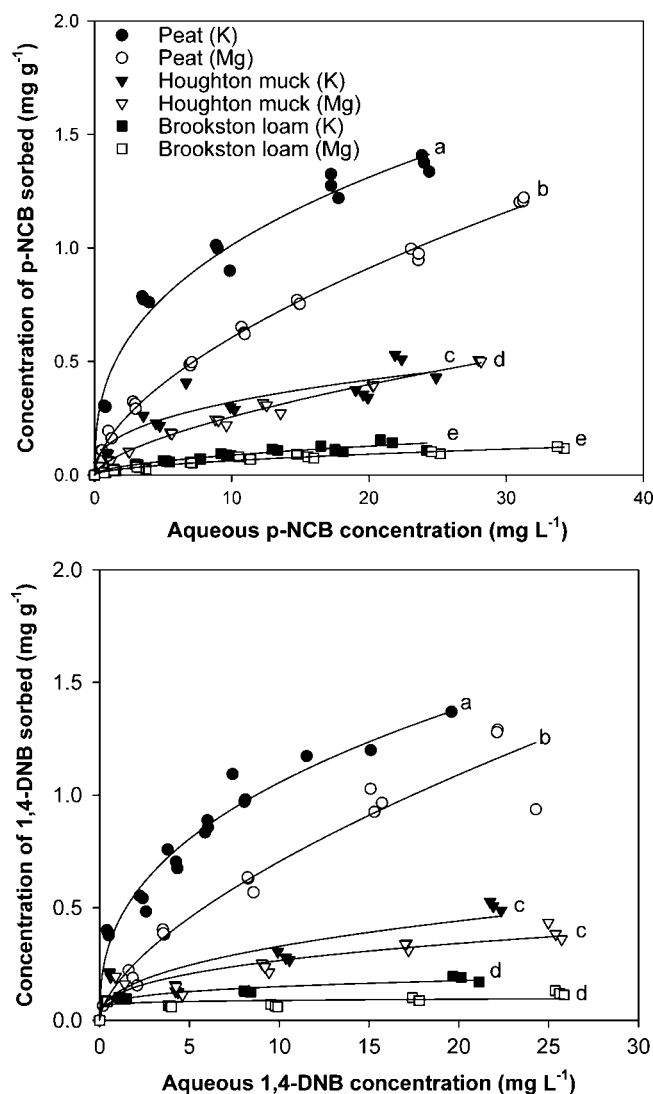
Fig. 5. Sorption isotherms for sorption of p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) by K^+- and Mg^{2+}–saturated Pahokee peat, Houghton muck, and Brookston loam. Isotherms with different letters (a, b, c, d, e) represent statistical difference at $p < 0.05$.

narrow ranges (less than threefold) of 0.56 to 1.07 and 0.56 to 1.36 mg g^{-1} for p-NCB and 1,4-DNB, respectively (Table 3); for p-NCB and 1,4-DNB sorption by Mg^{2+}–saturated peat, HM, and BL the Q_{om} values ($C_e = 5$ mg L^{-1}) fell within narrower ranges (less than twofold) of 0.38 to 0.55 and 0.47 to 0.62 mg g^{-1}, respectively (Table 3). These results suggest that as a sorbent phase for p-NCB and 1,4-DNB, SOM in PP, HM, and BL functions similarly. Comparison of p-NCB and 1,4-DNB sorption by each K^+– and Mg^{2+}–saturated test soil (peat, muck, and loam) reveals that the Q_{om} values were within a factor < 2 of each other (Table 3). This, again, is within the normal variation of K_{om} values observed among different soils (Kile et al., 1995) suggesting that SOM functioned very similarly as a sorbent phase regardless of whether the saturating cation was K^+ or Mg^{2+}. Our results therefore provided evidence that, in systems where sorption is dominated by SOM,

sorption of organic solutes is not strongly influenced by K^+ vs. Mg^{2+} as the saturating cation, as compared with that by soil mineral fractions. Among the group of solutes and soils characterized in this study it appears that differences in sorption induced by different cations saturating the CEC would result predominantly from their effect on the sorptive characteristics of the clay-sized mineral fraction and not SOM (see below).

X-ray diffraction analysis indicated that the minerals present in the clay fraction of the WA soil included kaolinite (3%), quartz (1%), smectite (24%), and mica and/or illite (3%); the clay fraction of the WB soil included kaolinite (2%), quartz (11%), smectite (16%), and mica and/or illite (2%) (Fig. 1). Sorption of p-NCB by K^+–saturated kaolinite, illite, montmorillonite (SWy-2), and beidellite showed that the smectite clays (i.e., montmorillonite and beidellite) were by far the most effective; montmorillonite was greater than two times more effective than beidellite (at 5 mg L^{-1}) (Fig. 6). These results agree with previous studies that report sorption affinities and capacities of clays for NACs increased in the order kaolinite < illite << montmorillonite (Haderlein et al., 1996). Thus, among the soil minerals present in the soils studied, smectites appear to be the dominant sorptive phase for NACs.

Previous studies have demonstrated that for pure smectite samples NAC sorption is affected strongly by the type of exchangeable cation (Boyd et al., 2001; Haderlein et al., 1996; Johnston et al., 2001, 2002; Li et al., 2003; Sheng et al., 2001, 2002; Weissmahr et al., 1997) Isotherms for NAC sorption by soil clay-sized fractions of the Webster soil samples were nonlinear and generally exhibited saturation-type curvature approaching a maximum surface concentration (Fig. 7), similar in shape to NAC sorption isotherms for pure smectites (Boyd et al., 2001). Concentrations of sorbed p-NCB on the different homoionic clay-sized fractions of the WA horizon soil
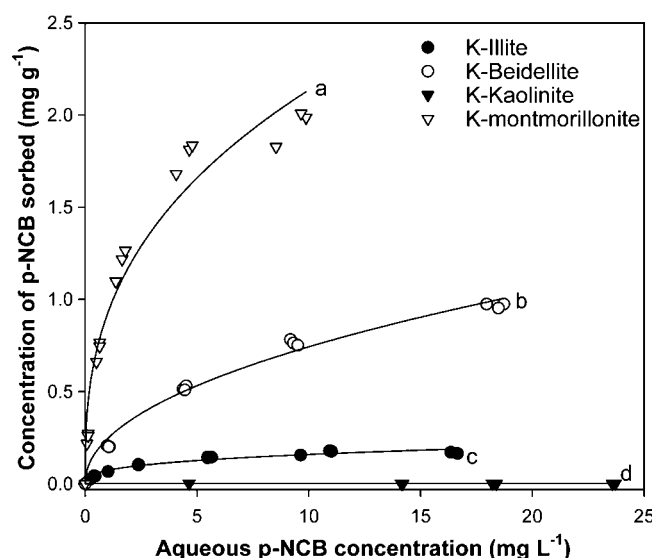

Fig. 6. Sorption isotherms for p-nitrocyanobenzene (p-NCB) by K^+–saturated reference clays (kaolinite, illite, beidellite, and montmorillonite). Isotherms with different letters (a, b, c, d) represent statistical difference at $p < 0.05$.
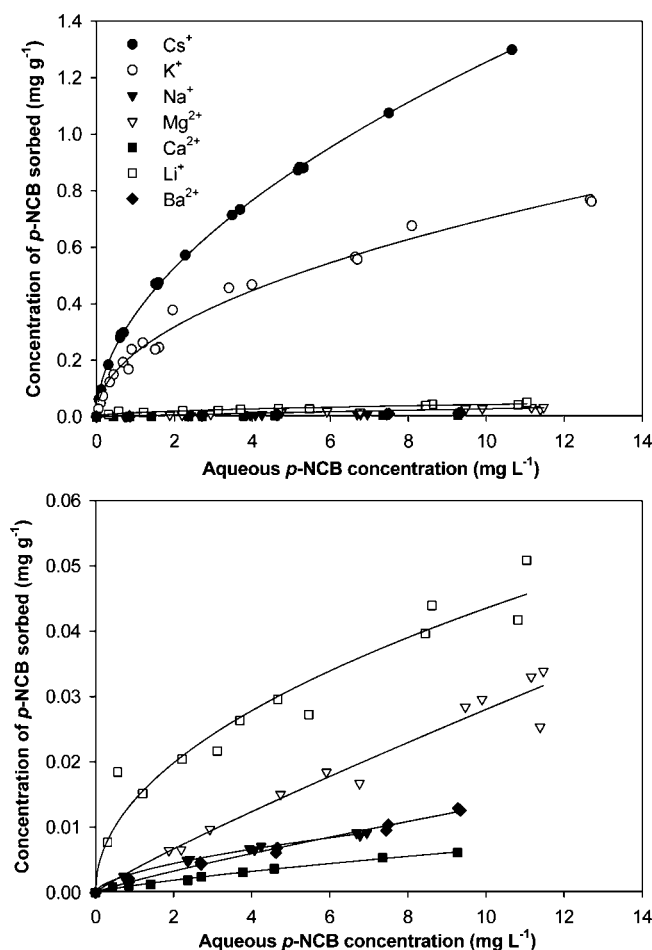
Fig. 7. Sorption isotherms for p-nitrocyanobenzene (p-NCB) by clay-sized fractions of the Webster A horizon soil exchanged with various cations (Cs^+, K^+, Na^+, Li^+, Ba^{2+}, Mg^{2+}, or Ca^{2+}).

were calculated (at $C_e = 5$ mg L^{-1}) using the results from the Freundlich equation fittings (Table 4). This comparison reveals that sorption of p-NCB generally increased in accordance with decreasing hydration energy, that is, $Na^+ < Li^+ < K^+ < Cs^+$ and $Ca^{2+} < Ba^{2+} < Mg^{2+}$ (Table 5; Fig. 7). Overall, Cs^+ and K^+–exchanged soil clays were much more effective sorbents than Na^+, Li^+, Ca^{2+}, Mg^{2+}, or Ba^{2+}–exchanged soil clays. These results are consistent with previous results that showed higher NAC sorption by reference smectites saturated with more weakly hydrated cations. Haderlein et al. (1996) and

Haderlein and Schwarzenbach (1993) found the extent of sorption of NACs was greater for K^+ and NH_4^+–clays compared with Al^{3+}, Ca^{2+}, Mg^{2+}, and Na^+–clays (Arizona montmorillonite and kaolinite). Similar results were obtained by Weissmahr et al. (1997, 1999) for NAC sorption to various reference minerals (illite, kaolinite, and Arizona montmorillonite). Sheng et al. (2002) measured 4,6-dinitro-o-cresol (DNOC) sorption to SWy-2 smectites and observed that K^+ and Cs^+–exchanged SWy-2 clays sorbed DNOC more effectively than Al^{3+}, Ba^{2+}, Ca^{2+}, or Na^+–exchanged SWy-2 reference clays.

Sorption of NACs by smectites occurs largely on the clay interlayers, and cation hydration determines the interlayer distance, size of adsorption domains, and the ability of NO_2 groups to complex directly with exchangeable cations (Boyd et al., 2001). Considering the hydrated radii of Cs^+, K^+, Na^+, Li^+, Ba^{2+}, Ca^{2+}, and Mg^{2+} (3.6, 5.3, 7.9, 10.0, 8.8, 9.6, and 10.8 Å, respectively) (Evangelou, 1998), it is apparent that lower cation hydration holds a smaller hydration sphere, thereby leaving larger siloxane surface domains, unobscured by water of hydration, for sorption. Large hydration spheres and strongly held hydration waters would also act to inhibit the direct interaction of NO_2 groups with the interlayer cation, as proposed by Boyd et al. (2001), Johnston et al. (2001, 2002) and Li et al. (2004b). Water molecules in the primary hydration sphere are less strongly held (lower enthalpy of hydration) by ions with larger ionic radii (e.g., K^+) compared with ions with smaller ionic radii (e.g., Na^+) or higher valence. These factors help account for the greater p-NCB sorption by Cs^+– and K^+–exchanged soil clay fractions (ionic radii 1.65 and 1.33 Å; ΔH_{hyd} -258 and -304 kJ mol^{-1}, respectively) compared with that by soil clay fractions exchanged with Na^+, Li^+, Ca^{2+}, Mg^{2+}, or Ba^{2+} (ionic radii, 0.98, 0.68, 1.17, 0.89 or 1.49 Å; ΔH_{hyd}, -375, -481, -1515, -1838, or -1258 kJ mol^{-1}, respectively).

The effect of cation hydration energy on sorption can be illustrated by comparing soil clays saturated with K^+ versus Ba^{2+}. Although these ions have similar ionic radii, at an equilibrium concentration of 5 mg L^{-1}, the K-exchanged soil clay fraction sorbed p-NCB to a much greater extent (69 times greater) than it did when exchanged with Ba^{2+} (Table 5). The larger hydration sphere and greater hydration energy of the Ba^{2+} ion (8.8 Å and -1258 kJ mol^{-1}) compared with the K^+ ion (5.3 Å and -304 kJ mol^{-1}) suggests that ion-dipole interactions between the exchangeable cation and polar functional groups on the NAC would require the displacement of more strongly held water molecules in the Ba^{2+}–exchanged system. The removal of water requires energy and so, for direct cation-solute interactions, the Ba^{2+}–exchanged system would require a larger energy input than the K^+–exchanged system. Related Fourier transform infrared spectroscopy studies observed-NO vibrational band shifts for 1,3,5-TNB sorption on K^+–smectite but not for Ba^{2+}–smectite (Boyd et al., 2001; Johnston et al., 2001, 2002).

The K-clays may also be more effective sorbents because K-clay interlayer spacings are expected to be

Table 4. Freundlich sorption equation K_f [(mg g^{-1})(mg L^{-1})$^{-n}$] and n values for p-nitrocyanobenzene sorption by the homoionic Webster A horizon soil clay-sized fraction and the whole soil. The Freundlich equations are graphed in Fig. 7 and 8.

Cation	Clay-sized fraction, <2 μm		Whole soil	
	K_f	n	K_f	n
Cs^+	0.363	0.539	0.096	0.467
K^+	0.226	0.490	0.053	0.598
Na^+	0.003	0.577	0.006	0.599
Li^+	0.014	0.488	0.008	0.634
Ba^{2+}	0.002	0.863	0.006	0.737
Mg^{2+}	0.004	0.892	0.007	0.622
Ca^{2+}	0.001	0.773	0.007	0.669

Table 5. Amount of p-nitrocyanobenzene sorbed per unit mass of sorbent (Q, calculated at C_e = 5 mg L^{-1} using the Freundlich sorption isotherms of Table 4) for sorption by the homoionic clay-sized fraction and the whole Webster A horizon soil. Q values are also normalized to lowest Q value among the monovalent and divalent homoionic soils.

Cation	Free Energy of Hydration, kJ mol^{-1}†	Smectite surface area available for sorption‡ %	Clay-sized fraction, <2 μm		Whole soil	
			Q, mg kg^{-1}	Q normalized to lowest Q	Q, mg kg^{-1}	Q normalized to lowest Q
Cs$^+$	−258	83	863.94	114.1	203.13	13.0
K$^+$	−304	64	498.40	65.8	138.25	8.9
Na$^+$	−375	21	7.57	1.0	15.57	1.0
Li$^+$	−481	−27	31.04	4.1	21.27	1.4
Ba^{2+}	−1258	51	7.22	1.9	19.46	1.1
Mg^{2+}	−1838	42	15.12	4.0	18.27	1.0
Ca^{2+}	−1515	26	3.82	1.0	20.83	1.1

† Y. Marcus. 1985. (p.107–109).
‡ Based on hydrated radii of cations, an average smectite surface area of 750 m^2 g^{-1}, an average cation exchange capacity of 100 cmol(+) kg^{-1}.

smaller than those of Ba-clays (MacEwan and Wilson, 1980), implying that sorption to the K-clays would be favored by a stronger contribution from hydrophobic interactions (Chappell et al., 2005). Li et al. (2004b) measured NAC adsorption enthalpies and used these to estimate enthalpies of NAC-smectite interactions. Their analyses considered several energy consuming or yielding processes including water removal from the clay and partial dehydration of the solute in the interlayer. The interaction energies between K-smectite and 1,3,5-TNB, 1,3-dinitrobenzene (1,3-DNB) and 1,4-DNB at 80% dehydration of the solute were −99, −69, and −73 kJ mol^{-1}, respectively. The calculated enthalpies of interaction between Ca^{2+}–exchanged SWy-2 and these NACs were lower ranging from −30 to −38 kJ mol^{-1}. Interlayer cation hydration directly affects interlayer spacing which in turn affects the interaction enthalpies discussed above. For example, Cs$^+$ and K$^+$–saturated smectites manifest interlayer spacings (d_{001}) near 12.3 Å in the presence of sorbed NACs, and this distance appears optimal for sorption of planar NACs (Li et al., 2004b; Sheng et al., 2001, 2002). These spacings correspond to interlayer thicknesses near 3 Å, which closely match the molecular thickness of p-NCB (Boyd et al., 2001). Adsorbed NACs in clay interlayers would then interact simultaneously with both opposing siloxane sheets, causing significant dehydration of the organic solute. Li et al. (2004b) estimated 80% dehydration in the interaction enthalpy calculation above, which is an energetically favorable process for a hydrophobic molecule. Smectites saturated with the other cations (e.g., Na$^+$, Ba^{2+}, Ca^{2+}) always swell to >15 Å in the presence of bulk water. For these cations, the energy required for interlayer compression and solute dehydration may be larger than the energy gained from solute dehydration, thereby, making the overall process energetically less favorable compared to Cs$^+$ and K$^+$-saturated smectites. The extent of p-NCB sorption to Mg-, Ca-, and Ba-soil was small and relatively independent of differences among divalent cations (Table 5, Fig. 8), which all seem to bind water too strongly to allow (a) lateral sorption domains on smectite basal surfaces and/or (b) narrow d_{001}–spacings that enhance hydrophobic interactions.

The effects of saturating cation on sorption of p-NCB by whole soils were similar to those by the isolated soil clay-sized fractions. Sorption of p-NCB by Cs$^+$– and K$^+$–saturated soils was again much higher than by the divalent-cation-exchanged soils (Table 5; Fig. 7 and 8). The weakly sorbing systems (homoionic Li$^+$–, Na$^+$–, Mg^{2+}–, Ca^{2+}–, or Ba^{2+}–WA horizon soil) were more tightly bunched (Fig. 8) than they were after SOM removal (Fig. 7). Q_{om} values for p-NCB sorption at C_e = 5 mg L^{-1} (Table 3) show that about 75% of the total sorption to these weakly sorbing systems (Table 5, Fig. 8)
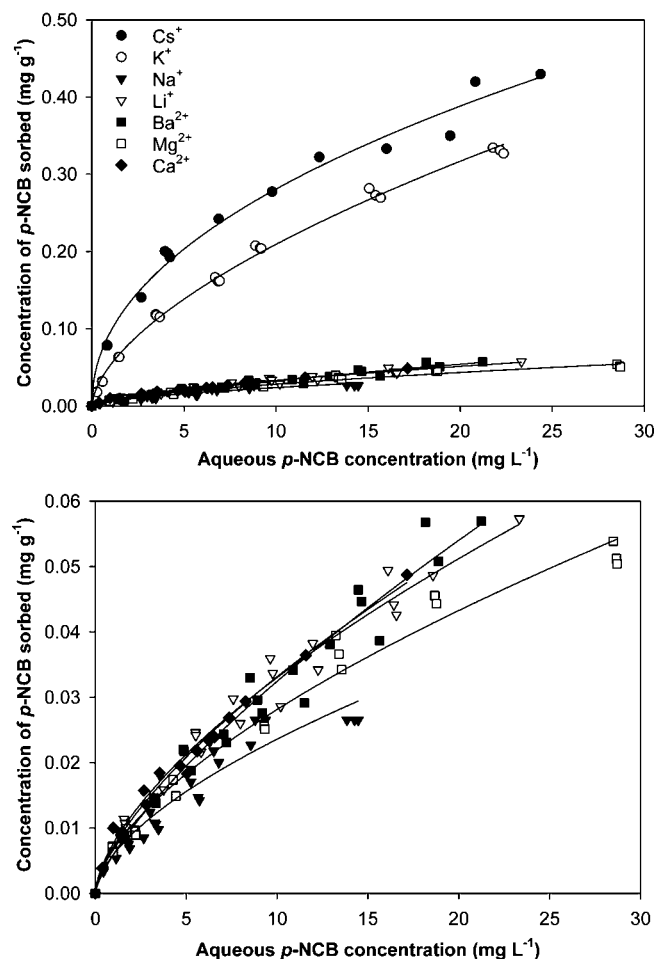
Fig. 8. Sorption isotherms for p-nitrocyanobenzene (p-NCB) by the Webster A horizon soil exchanged with various cations (Cs$^+$, K$^+$, Na$^+$, Li$^+$, Ba^{2+}, Mg^{2+}, and Ca^{2+}).

is attributable to SOM so that differences due to smectites are less apparent in the whole soils.

However, for the strongly sorbing Cs^+– and K^+–saturated WA horizon whole soil, sorption (at $C_e = 5$ mg L^{-1}) to the soil clay-sized fraction (Table 5) was 9 to 13 times sorption by SOM (Table 3). As noted in conjunction with Fig. 2 and 3 above, the chief effect of SOM in these systems was not to sorb NACs, but to suppress NAC sorption by the soil clays. These results suggest that NAC sorption to Cs^+– or K^+–saturated whole Webster soil samples is dominated by sorption to soil clays, primarily smectite clays. While Cs^+– or K^+–saturated soils would be rare in the environment, sorption of pesticides has been shown (Li et al., 2004a) to increase with K^+ addition to Ca^{2+}–dominated systems, and substantial demixing of K^+ and Ca^{2+} results in K^+–saturated smectite interlayers when K^+ populates more than 40% of the cation exchange sites (Li et al., 2004a). Thus, K^+–saturated smectites could plausibly be formed through K^+ fertilization of Ca^{2+}–dominated soils like the Webster soil series, and these K-smectites would be strong sorbents for NACs. Furthermore, these systems, in which relatively hydrophobic compounds like NACs sorb more strongly to soil clays than they do to SOM, reveal that SOM apparently coats (or otherwise obscures) soil clay surfaces, thereby diminishing adsorption of NACs by the clay minerals in soil.

CONCLUSIONS

Sorption of NACs by the WA and WB was strongly influenced by the nature of the dominant exchangeable cation due to cation effects on the sorptive characteristics of soil smectite clays. The relationship between saturating cation and the observed p-NCB sorption order can be explained by cation hydration energy and its effect on the molecular-scale clay interlayer environment. Increasing the hydration energy of the exchanged cation decreased the extent of sorption of p-NCB by the clay-sized soil fraction and whole soil due to diminished effective size of adsorption domains between exchangeable cations, less favorable interactions between the exchange cation and NO_2 groups of sorbed NACs, and to greater interlayer separations which disallow solute dehydration. Exchangeable cation type did not strongly influence sorption of organic solutes by SOM. Thus, in soils lacking smectite clays, sorption of nonpolar organic solutes will probably not be strongly influenced by the type of exchangeable cation. Conversely, for organic solutes with polar functional groups (e.g., NO_2), and in soils containing smectite clays, solute uptake from water will be strongly influenced by the type of exchangeable cation(s) present. Greatest NAC retention would be anticipated in soils saturated with cations such as Cs^+, K^+, and NH_4^+. Organic matter coatings on soil clays may diminish the overall capacity of clays to adsorb NACs.

ACKNOWLEDGMENTS

REFERENCES

Boyd, S.A., G. Sheng, B.J. Teppen, and C.T. Johnston. 2001. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. Environ. Sci. Technol. 35:4227–4234.

Chappell, M.A., D.A. Laird, M.L. Thompson, H. Li, B.J. Teppen, V. Aggarwal, C.T. Johnston, and S.A. Boyd. 2005. Influence of smectite hydration and swelling on atrazine sorption behavior. Environ. Sci. Technol. 39:3150–3156.

Chiou, C. 2002. Partition and adsorption of organic contaminants in environmental systems. John Wiley & Sons, NJ.

Chiou, C., L. Peters, and V. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206:831–832.

Chiou, C., P. Porter, and D. Schmedding. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17:227–231.

Evangelou, V. 1998. Environmental soil and water chemistry: Principles and applications. John Wiley & Sons, New York.

Gee, G., and J. Bauder. 1986. Particle-size analysis. p. 383–411. In A. Klute (ed.) Methods of Soil Analysis. Part I. 2nd ed. Agron. Monogr. 9. ASA, Madison, WI.

Haderlein, S., and R. Schwarzenbach. 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces. Environ. Sci. Technol. 27:316–326.

Haderlein, S.B., K. Weissmahr, and R. Schwarzenbach. 1996. Specific adsorption of nitroaromatic: Explosives and pesticides to clay minerals. Environ. Sci. Technol. 30:612–622.

Howard, P., and W. Meylan. 1997. Handbook of physical properties of organic chemicals. Lewis Publishers, Boca Raton, FL.

Johnston, C., M.F. de Oliveira, B.J. Teppen, G. Sheng, and S.A. Boyd. 2001. Spectroscopic study of nitroaromatic-smectite sorption mechanisms. Environ. Sci. Technol. 35:4767–4772.

Johnston, C., G. Sheng, B.J. Teppen, S.A. Boyd, and M.F. de Oliveira. 2002. Spectroscopic study of dinitrophenol herbicide sorption on smectite. Environ. Sci. Technol. 36:5067–5074.

Karickhoff, S. 1984. Organic Pollutant Sorption in aquatic systems. J. Hydraul. Eng. 110:707–735.

Karickhoff, S., D. Brown, and T. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241–248.

Kile, D.E., C.T. Chiou, H. Zhou, H. Li, and O. Xu. 1995. Partition of nonpolar organic pollutants from water to soil and sediment organic matters. Environ. Sci. Technol. 29:1401–1406.

Kunze, G., and J. Dixon. 1986. Pretreatment for mineralogical analysis. p. 92–99. In A. Klute (ed.) Methods of Soil Analysis. Part I. 2nd ed. Agron. Monogr. 9. ASA, Madison, WI.

Laboski, C.A.M., and J.A. Lamb. 2004. Impact of manure application on soil phosphorus sorption characteristics and subsequent water quality implications. Soil Sci. 169:440–448.

Laird, D., Y. Yen, W. Koskinen, T. Steinheimer, and R. Dowdy. 1994. Sorption of atrazine on soil clay components. Environ. Sci. Technol. 28:1054–1061.

Li, H., G. Sheng, B. Teppen, C. Johnston, and S.A. Boyd. 2003. Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. Soil Sci. Soc. Am. J. 67:122–131.

Li, H., B.J. Teppen, D.A. Laird, C.T. Johnston, and S.A. Boyd. 2004a. Geochemical modulation of pesticide sorption on smectite clay. Environ. Sci. Technol. 38:5393–5399.

Li, H., B.J. Teppen, D. Laird, C. Johnston, and S.A. Boyd. 2004b. Thermodynamics of nitroaromatic compound adsorption from water by smectite clay. Environ. Sci. Technol. 38:5433–5442.

MacEwan, D.M.C., and M.J. Wilson. 1980. Interlayer and intercalation complexes of clay minerals. p. 197–248. In G.W. Brindley and G. Brown (ed.) Crystal structures of clay minerals and their X-ray identification, Mineralogical Society, London.

Marcus, Y. 1985. Ion solvation. John Wiley & Sons, New York.

Nelson, D., and L. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961–1010. In D. Sparks (ed.) Methods of Soil Analysis. Part III. SSSA Book Ser. No. 5. ASA and SSSA, Madison, WI.

SAS Institute. 1999. SAS 8.1. SAS Institute, Inc., Cary, NC.

Sheng, G., C.T. Johnston, B.J. Teppen, and S.A. Boyd. 2001. Potential contributions of smectite clays and organic matter to pesticide retention in soils. J. Agric. Food Chem. 49:2899–2907.

Sheng, G., C.T. Johnston, B.J. Teppen, and S.A. Boyd. 2002. Adsorption of dinitrophenol herbicides from water by montmorillonites. Clays Clay Miner. 50:25–34.

Sumner, M., and W. Miller. 1996. Cation exchange capacity and exchange coefficients. p. 1201–1229. *In* D. Sparks (ed.) Methods of Soil Analysis. Part III. SSSA Book Ser. No. 5. ASA and SSSA, Madison, WI.

Weissmahr, K., S. Haderlein, and R. Schwarzenbach. 1997. In Situ Spectroscopic investigations of adsorption mechanisms of nitro-

aromatic compounds at clay minerals. Environ. Sci. Technol. 31: 240–247.

Weissmahr, K., S. Haderlein, and R. Schwarzenbach. 1998. Complex formation of soil minerals with nitroaromatic explosives and other pi-acceptors. Soil Sci. Soc. Am. J. 62:369–378.

Weissmahr, K., M. Hildenbrand, R. Schwarzenbach, and S. Haderlein. 1999. Laboratory and Field Scale Evaluation of Geochemical Controls on Groundwater Transport of Nitroaromatic Ammunition Residues. Environ. Sci. Technol. 33:2593–2600.

Whittig, L., and W. Allardice. 1987. X-ray diffraction techniques. p. 338–342. *In* A. Klute (ed.) Methods of Soil Analysis. Part I. 2nd ed. Agron. Monogr. No. 9. ASA and SSSA, Madison, WI.